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Optimizing the conditions of mechanochemical synthesis of LiAl layered hydroxides

Stepanova L.N. [a,b] * , Belskaya O.B.[a,c], Baklanova O.N.[a], Vasilevich A.V.[a], Likholobov V.A.[a,c,d]

[a]*Institute of Hydrocarbons Processing SB RAS, 54 Neftezavodskaya St., Omsk 644040, Russian Federation*
[b]*F.M. Dostoevsky Omsk State University, 55a Mira Pr., Omsk 644077, Russian Federation*
[c]*Omsk State Technical University, 11 Mira Pr., Omsk 644050, Russian Federation*
[d]*Omsk Scientific Center SB RAS, 15 Karl Marx Pr., Omsk 644024, Russian Federation*

Abstract

LiAl layered double hydroxides (LDH) are the promising compounds for application in base catalysis and as precursors of the supports for platinum catalysts. In the work, such systems were synthesized by mechanochemical method. The effect of composition of the initial mixture ($Al(OH)_3$, $Al(NO_3)_3$, LiOH, $LiNO_3$), material of milling bodies (steel or ceramic), and activation conditions (centripetal acceleration and activation time) on the properties of LiAl-LDH were studied. It was found that each of the synthesized systems is a polyphase one and contains not only the LDH phase but also the side phase of aluminum trihydroxide. In addition, the samples obtained with the use of steel milling bodies have a substantial amount of iron. The use of ceramic milling bodies makes it possible to obtain the LiAl-LDH phase under relatively mild conditions (acceleration of 300 m/s^2 and activation time of 15 min).

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Keywords: mechanochemical activation, LiAl layered double hydroxides, rehydration of mixed oxides

* Corresponding author. Tel.: +7 (3812) 670474
*E-mail address:*Lchem@yandex.ru

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1. Introduction

Layered double hydroxides (LDH) form a class of inorganic compounds whose layers consist of cations of the metals with different valences (as a result, the layers are positively charged), and the interlayer space is filled with charge compensating anions and water molecules [1]. A general formula of LDH can be written as $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x\backslash n}\bullet mH_2O$, where M^{II} is a divalent metal, M^{III} is a trivalent metal, An- is an anion, and $x = M^{III}/(M^{III} + M^{II})$. In addition to di- and trivalent metals, some tetravalent metals (Sn and Zr) can also be incorporated into LDH layers. Among LDH with univalent cations, only the LiAl-LDH are known. A distinctive feature of LiAl-LDH is the increased basicity, which opens wide possibilities for their application as solid bases instead of alkalies in organic reactions catalyzed by bases (aldol condensation of furfural with acetone, isomerization of alkenes, the Michael addition reaction, etc.). Along with this, promising is the use of LiAl-LDH as the precursors of non-acid supports for platinum catalysts. The conventional method of LDH synthesis is coprecipitation [2]. It consists of a slow addition of metal salts to sodium carbonate at constant temperature and pH values. The subsequent ageing, washing, filtering and drying procedures lead to the formation of the end product. If some conditions are met (M^{II}/M^{III} = 2-4 and a less than 1.5-fold difference in the radii of cations), the synthesized LDH will have a homogeneous phase composition. A long-term synthesis and a large amount of wash water are the drawbacks of coprecipitation method. In addition, it is difficult to synthesize LiAl-LDH by this method. So, new methods should be devised in these fields in order to obtain LDH with the extended cationic composition (LiAl-LDH). To achieve this goal, the most promising method is mechanochemical synthesis.

Mechanochemical activation makes it possible to obtain LDH via a short-term synthesis and avoid a large amount of wash water, which are its advantages over the conventional coprecipitation method [3]. However, in order to obtain the pure LDH phase, an adequate selection of activation conditions is needed: the type of initial components, material of milling bodies, acceleration, activation time, etc. [4-7]. As it was demonstrated in our earlier study, the phase-homogeneous system cannot be obtained at a ratio of Al/Li = 2, acceleration of 300 – 1000 m/s^2, and activation time of 5-30 min [8]. Along with LiAl-LDH, the mechanically activated mixture contained a considerable amount of unreacted aluminum trihydroxide. In the present work, in order to provide a more complete use of aluminum hydroxide, the maximum possible severity of the synthesis conditions was created. In addition, syntheses were performed using the mixtures with a decreased content of aluminum hydroxide.

2. Experimental

2.1. LiAl- LDH synthesis by mechanochemical activation

The synthesis of LiAl-LDH was carried out in a planetary AGO-2 mill with steel or ceramic milling bodies (balls) at room temperature and atmospheric pressure. In all the experiments, the weight ratio of milling bodies to mechanically activated mixture was constant and equal to 40:1. Depending on the ball material, different initial mixtures were employed; activation conditions (centripetal acceleration of milling bodies and activation time) were also varied. The samples synthesized from lithium nitrate and aluminum hydroxide with the use of steel and ceramic balls are denoted, respectively, as NH-Fe and NH-Zr, whereas the samples synthesized from lithium and aluminum hydroxides with the use of steel balls are denoted as HH-Fe. The chemical composition of the mixture and the activation conditions for each sample of these two series (with steel and ceramic balls) are listed in Table 1.

Table 1. Chemical composition of initial components and conditions of LiAl-LDH synthesis with the use of steel and ceramic balls.

Sample	Material of milling bodies	Initial compounds*	Al/Li ratio	Activation time, min	Acceleration, m/s^2
NH-Fe-1	Steel	$Al(OH)_3$+ $Li(NO_3)_3\bullet 3H_2O$	2	60	1000
NH -Fe-2		$Al(OH)_3$+ $Li(NO_3)_3\bullet 3H_2O$	1	60	
NH -Fe-3		$Al(NO_3)_3\bullet 9H_2O$+ LiOH	1	30	

HH-Fe-1		$Al(OH)_3$+ LiOH	1	30	
NH-Zr-1	Ceramic	$Al(OH)_3$+ $Li(NO_3)_3$•$3H_2O$	2	15	300
NH-Zr-2		$Al(OH)_3$+ $Li(NO_3)_3$•$3H_2O$	2	30	
NH-Zr-3		$Al(OH)_3$+ $Li(NO_3)_3$•$3H_2O$	2	60	

* Al(OH)3 was represented by gibbsite

2.2. Synthesis of 'activated' LiAl-LDH

To obtain the activated form of LiAl-LDH (LDH with OH^- anions in the interlayer space), the initial LiAl-LDH with CO_3^{2-} was calcined in a muffle furnace at 600 °C for 3 h. The resulting $LiAlO_x$ mixed oxide was rehydrated in distilled water for 8 h at room temperature and then dried in a drying oven at 120 °C for 12 h.

2.3. Measurement of Fe and Zr content in LiAl-LDH

The content of iron and zirconium in the synthesized samples was measured after their preliminary dissolution by means of inductively coupled plasma atomic emission spectrometry on a Varian 710-ES instrument and by atomic absorption spectroscopy on an AAS 6300 (Shimadzu) device.

2.4. Investigation of the structural properties of LiAl-LDH

The structural properties of the synthesized LDH were examined using X-ray diffraction analysis (XRD). The XRD studies were carried out on a D8 Advance (Bruker) diffractometer with parallel Cu-Kα source in a 2θ range from 5 to 80°. The scanning step was 0.05°, and the time of signal integration, 5 s/step. Phase composition of the samples was identified using the ICDD PDF-2 International database.

2.5. Investigation of the formation of the $LiAlO_x$ oxide phase

Thermal decomposition of the samples was studied on an STA-449C Jupiter (Netzch) instrument conjugated with an QMS-403C Aeolos quadrupole mass spectrometer via the capillary heated to 300 °C. The measurements were made under dynamic mode in air at a heating rate of 10 °/min. Weight of the samples was 10-20 mg.

2.6. Investigation of textural properties

Textural properties (specific surface area, pore size and volume) of LiAl mixed oxides (LDH calcined at 600 °C) were examined by the low-temperature nitrogen adsorption. Nitrogen adsorption-desorption isotherms were measured at 77.4 K in a volumetric vacuum static setup ASAP-2020 (Micromeritics). The equilibrium relative pressures ranged from 10^{-3} to 0.996 P/P_0. The BET specific surface area (S_{BET}) was calculated in the region of equilibrium relative values of nitrogen vapor, P/P_0 = 0.05-0.25, using the adsorption isotherm. In the calculation of specific surface area, the molecular nitrogen site in the filled monolayer was assumed to be 0.162 nm^2. The adsorption pore volume (V_{ads}) was found from the nitrogen adsorption at P/P_0 = 0.990 under the assumption that density of the adsorbate is equal to the density of normal liquid, 0.02887 mol/cm^3. The average pore diameter was estimated by the formula $D = 4V_{ads}/S_{BET}$. Differential characteristics of the pore size distribution curves were obtained by applying the BJH method to the desorption branch of the isotherms. The calculation was performed within the cylindrical model of unconnected pores.

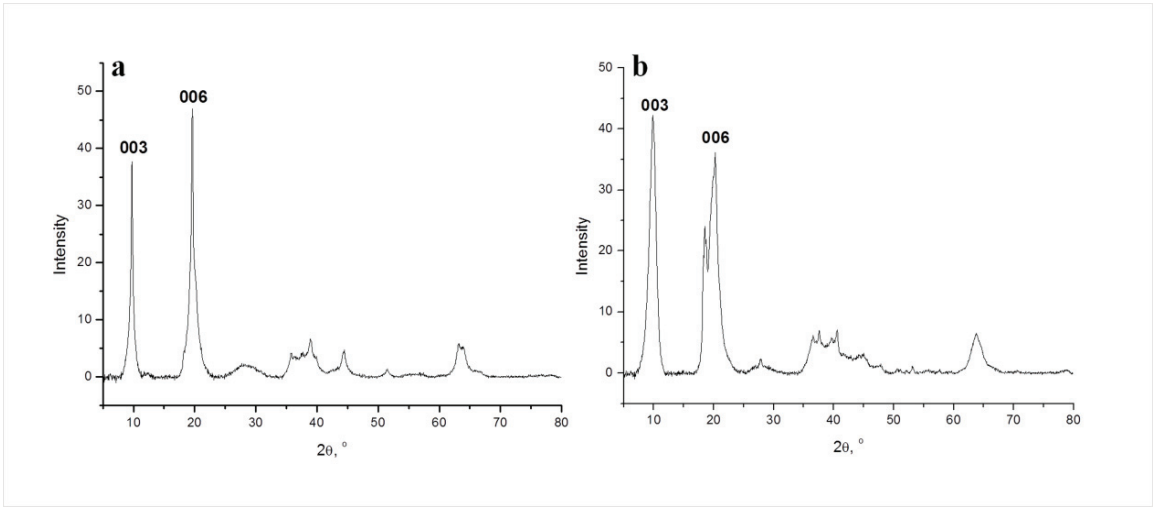
3. Results and discussion

3.1. Investigation of the properties of LiAl-LDH samples obtained with the use of steel balls as the milling bodies

The use of steel balls, which possess high mechanical strength, as the milling bodies in the synthesis of samples by mechanochemical activation is a traditional and widely used approach. Their application allows the activation to be performed at a high acceleration, which ensures the most complete reaction of the initial components. In this work, the effect of the Al/Li ratio and chemical composition of the initial mixture on the properties of resulting compounds was revealed for LiAl-LDH samples synthesized with the use of steel milling bodies.

To elucidate the effect of Al/Li ratio on the properties of LiAl-LDH produced by mechanochemical activation, gibbsite ($Al(OH)_3$) and lithium nitrate ($Li(NO_3)_3 \cdot 3H_2O$) were chosen as the initial compounds. The Al/Li ratio was equal to 1 and 2. The mixture was activated at a maximum possible centripetal acceleration of milling bodies (1000 m/s^2) for this variant of instrumentation, and at a long activation time (60 min).

According to the XRD data, the formation of the LDH phase with a typical set of reflections in the region of low, medium and high angles is observed for NH-Fe-1 and NH-Fe-2 samples irrespective of the Al/Li ratio (Fig. 1).



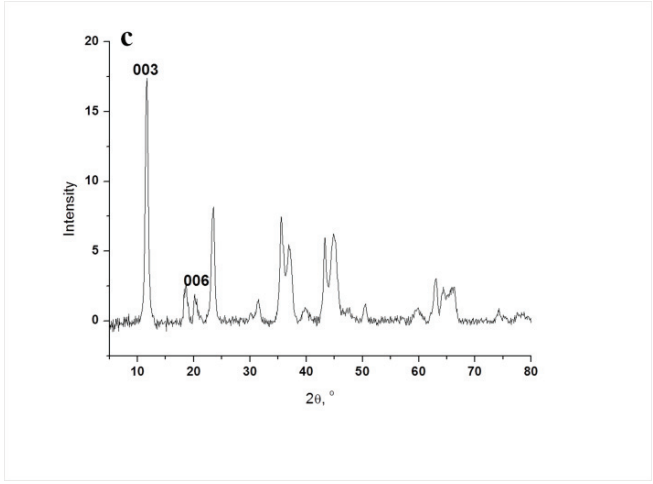


Fig. 1. Diffraction patterns of LiAl-LDH: (a) NH-Fe-1, (b) – NH-Fe-2, (c) HH-Fe-1.

An increase in the aluminum content of LiAl-LDH slightly decreases the interplanar distance d003 and, accordingly, the lattice parameter c (Table 2). However, not only the main LDH phase is observed on the diffraction patterns but also the reflections typical of the initial aluminum trihydroxide. Evidently, a complete conversion of $Al(OH)_3$ does not take place under the chosen conditions of mechanochemical activation, and some fraction of this compound is present in the composition of LDH as unreacted aluminum trihydroxide. The XRD calculations performed by the tag method [9] allowed estimating the fraction of unreacted gibbsite as 6.5 and 2.1 wt.% for LDH with Al/Li = 2 and 1, respectively. As the Al/Li ratio is raised, the amount of $Al(OH)_3$ increases nearly threefold (Table 2). The chemical analysis of NH-Fe-1 and NH-Fe-2 revealed the presence of iron in the samples, which could be produced by attrition of steel balls during mechanical activation. With an increase in the Al/Li ratio, the amount of iron decreases twofold (Table 2).

Table 2. Lattice parameters for NH-Fe-1 and NH-Fe-2 samples and the content of side components.

Sample	Al/Li	d_{006}, Å	c, Å	$Al(OH)_3$ content, wt.%	Fe content, wt.%
NH-Fe-1	2	9.06	27.18	6.5	1.1
NH-Fe-2	1	9.12	27.36	2.1	2.1

The NH-Fe-3 sample, which was synthesized from aluminum nitrate and lithium hydroxide as the initial compounds, was found to be X-ray amorphous. This is why it was excluded from the study. The HH-Fe-1 sample ($Al(OH)_3$ and LiOH as the initial compounds) was found to be a polyphase one, similar to the other samples (Fig. 1c). However, its iron content exceeded the corresponding values for other samples and was equal to 19 wt.%.

Thus, even under the most severe conditions created with the use of steel milling bodies, the phase-homogeneous system was not obtained. Therewith, a substantial amount of the iron oxide admixture appeared in the composition of the sample. So, it was reasonable to employ another material for milling bodies – ceramic balls. At the same time, the application of ceramic balls limits the acceleration to 300 m/s^2 and allows the depth of reaction to be controlled only by the contact time.

3.2. Investigation of the properties of LiAl-LDH samples synthesized with the use of ceramic balls as the milling bodies

Mechanochemical activation with ceramic milling bodies produced LiAl-LDH with Al/Li = 2. Aluminum hydroxide ($Al(OH)_3$) and lithium nitrate ($Li(NO_3)_3 \bullet 3H_2O$) served as the initial compounds. To synthesize three LiAl-LDH samples, the mixture was activated at a constant acceleration of 300 m/s^2 for different times: 15, 30 and 60 min (Table 1). As it was noted above, the low acceleration was used because ceramic balls are quite brittle.

The study of structural properties of the synthesized LiAl-LDH showed that the LDH phase with the typical basal reflections 003 and 006 is formed even at a minimum activation time used in the work (Fig. 2). The LDH bands in the region of medium (012, 015, 018) and high (110 and 113) angles are strongly smeared. Such smear may be related to the formation of the turbostratically disordered phase of LiAl-LDH.

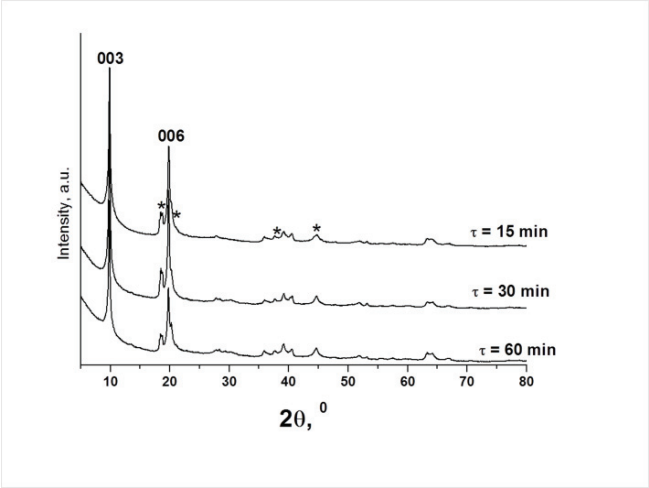


Fig. 2. Diffraction patterns of LiAl-LDH synthesized with the use of ceramic milling bodies at different activation times. An acceleration of 300 m/s^2. * – the $Al(OH)_3$ phase.

Table 3. Lattice parameters for the samples synthesized with the use of ceramic milling bodies, and textural characteristics of their calcined species.

Sample	d_{003}, Å	c, Å	a, Å	S_{BET}, m^2/g	V_{pore}, cm^3/g
NH-Zr-1	8.54	25.61	2.916	92	0.338
NH-Zr-2	8.98	26.93	2.934	97	0.345
NH-Zr-3	9.00	26.99	2.937	103	0.441

Similar to the samples from the first series (obtained with the use of steel balls), the LiAl-LDH samples synthesized with the use of ceramic balls also have a polyphase composition, which means that they contain not only the main phase but also the aluminum trihydroxide phase (the peaks corresponding to the side phase are marked with asterisks on Fig. 2). The amount of unreacted gibbsite constitutes ca. 30 mol.% of the initial $Al(OH)_3$. An extension of the activation time increases the interplanar distance d_{003} and, accordingly, the lattice parameter *c*. A minor increase in the lattice parameter *a* when moving to more severe conditions of the synthesis indicates a decrease in the number of aluminum atoms in LDH layers. According to the chemical analysis data, the content of zirconium in the resulting samples, which appears due to attrition of ceramic milling bodies, does not exceed 0.5 wt.%.

The formation of the $LiAlO_x$ oxide phase was studied by thermal analysis. The DTG profiles of LiAl-LDH, which were obtained under different activation conditions, were identical.

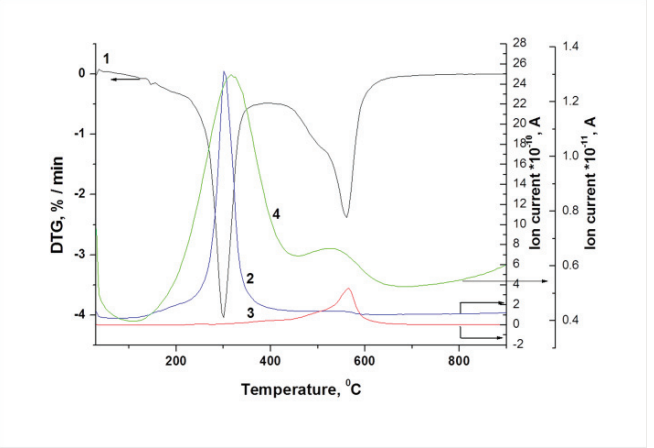


Fig. 3. The DTG curve (1) and mass spectra of decomposition products: H2O, m/z = 18 (2); NO, m/z = 30 (3), CO2, m/z = 44 (4) for the NH-1 sample. Mass spectra are presented in the standard 'temperature – ion current' coordinates.

Three main regions of weight loss can be distinguished on DTG profiles of NH-Zr samples (Fig. 3). The low-temperature region (below 230 C) corresponds to removal of the interlayer and adsorbed water. The high-temperature region (450 – 600 °C) is responsible for dehydroxylation and removal of interlayer anions; these processes occur simultaneously, which produces a shoulder at 490 °C. A weight loss in the region of 300 °C corresponds to the formation of alumina from unreacted $Al(OH)_3$, which was presented in each of the synthesized samples. The analysis of the mass spectra of decomposition products confirms that the temperature maximum at 300 C corresponds to a release of water and carbon dioxide (which is probably adsorbed from air). A small amount of water is released also in the region of 450 – 500 °C, which may be related to dehydroxylation of the brucite-like layers. The high-temperature weight loss maximum corresponds to the release of nitrogen oxide, which testifies to the presence of nitrate anions in the interlayer space of LiAl-LDH (Fig. 3).

Textural properties of $LiAlO_x$ mixed oxides, which were produced by calcination of LiAl-LDH at 600 C, also depend on the conditions of mechanochemical activation. The shape of nitrogen adsorption-desorption isotherm for all mixed oxide samples corresponds to the IV type isotherm with a hysteresis loop typical of mesoporous materials. An extension of the activation time produces a small increase in specific surface area and pore volume (Table 3). In addition, the extended activation time shifts the maximum on the pore size distribution curves toward greater values of pore diameters (Fig. 4).

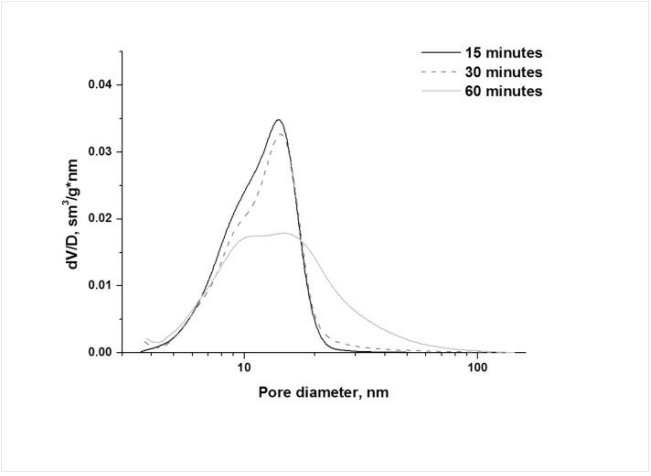


Fig. 4. Pore size distribution curves for NH-Zr samples synthesized at different activation time.

An important property of the system of LiAl-Zr samples was investigated – the possibility of rehydration of the corresponding mixed oxides, i.e. the restruction of the layered structure upon holding of $LiAlO_x$ in water. Restruction of the structure upon rehydration opens great possibilities not only for anionic exchange and anchoring of the active component precursor on the external surface of the support but also for its introduction directly in the interlayer space, which would lead to the formation of active sites with different catalytic properties.

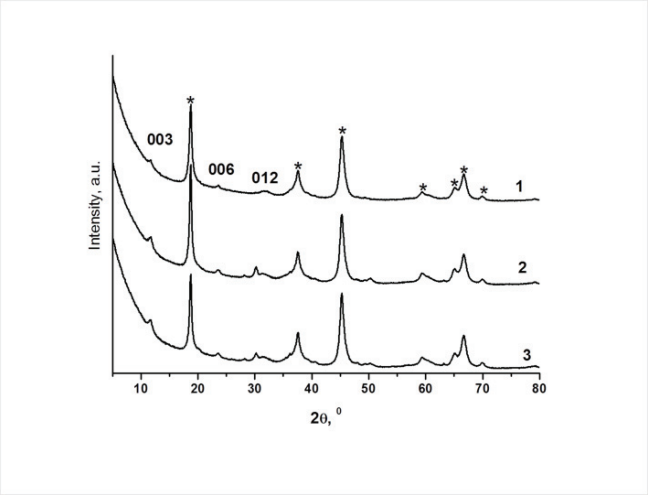


Fig. 5. The diffraction pattern of LiAl-LDH rehydrated under different conditions of the synthesis of initial LDH: 1 – 15 min, 2 – 30 min, 3 – 60 min. * – $LiAlO_2$.

According to XRD data for the samples obtained after rehydration of $LiAlO_x$ in water, all lithium-containing mixed oxides are able to restore their structure, which confirms the appearance of basal reflections on the diffraction patterns of rehydrated samples (Fig. 5).

4. Conclusion

The study demonstrated that the application of ceramic milling bodies makes its possible to obtain the aluminum-lithium LDH phase under relatively mild conditions of mechanochemical synthesis. Although, similar to the case of steel balls, the phase-homogeneous system was not produced under the chosen conditions of synthesis, the amount of impurity cations (zirconia) considerably decreased. It was found that the synthesized LDH have the memory effect and can restore their layered structure after calcination, which is an important property that should be taken into account in the synthesis of supported catalysts. The oxide phases obtained from LiAl-LDH possess a developed pore space and can be considered as the promising supports for non-acid catalysts.

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